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# Extraordinary Coordination of Acetonitrile to Square-Planar, 1,4,8,11-Tetraazacyclotetradecanenickel(II) and (1*R*,4*R*,8*S*,11*S*)-1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecanenickel(II) Cations

Takashi Yokoyama, Etsuro Iwamoto, and Takahiro Kumamaru*
Department of Chemistry, Faculty of Science, Hiroshima University,
Higashisenda-machi, Naka-ku, Hiroshima 730
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Coordination of dipolar aprotic solvents to the square-planar complexes of nickel(II) was investigated in nitrobenzene (NB) spectrophotometrically. Compared with *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), it was observed that acetonitrile (AN) was strongly coordinated to $[NiL]^{2+}$ (L=1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane). The stepwise coordination constants $K_{NiS1}$ and $K_{NiS2}$ ($mol^{-1}$ $dm^3$) for (1*R*,4*R*,8*S*,11*S*)-$[NiL]^{2+}$ were found to be (1.6, 0.5), (1.0, 0.1), (3.4, 6.7), and (0.4, 1.9) for DMSO, DMF, AN, and benzonitrile, respectively. The $K_{NiS2}$ values for nitriles are larger than the $K_{NiS1}$ values, showing that nitriles are coordinated to the metal ion through π-back donation.

$[NiL]^{2+}$ (L=1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) has two stable isomer of 1*R*,4*R*,8*S*,11*S*-nitrogen and 1*R*,4*S*,8*R*,11*S*-nitrogen configuration.[1–9] $[Ni(cyclam)]^{2+}$ (cyclam=1,4,8,11-tetraazacyclotetradecane), (1*R*,4*R*,8*S*,11*S*)-$[NiL]^{2+}$ and (1*R*,4*S*,8*R*,11*S*)-$[NiL]^{2+}$ are described in Scheme (1). (1*R*,4*R*,8*S*,11*S*)-$[NiL]^{2+}$ and $[Ni(cyclam)]^{2+}$ form the six-coordinated complexes where two solvent molecules are attached to the central nickel.[9,10] However, (1*R*,4*S*,8*R*,11*S*)-$[NiL]^{2+}$ forms the five-coordinated complex where only one solvent molecule is attached to the nickel.[7] The rate constants for exchange reaction of the coordinated solvent have been reported in $H_2O$, acetonitrile(AN), and *N,N*-dimethylformamide (DMF).[11–14] Accordingly, the observed values of enthalpy of activation for (1*R*,4*R*,8*S*,11*S*)-$[NiL]^{2+}$ were about twice as large as those for (1*R*,4*S*,8*R*,11*S*)-$[NiL]^{2+}$. It was also found that the coordination of the AN molecule to both isomers of $[NiL]^{2+}$ is stronger than that of other basic solvents.[14]

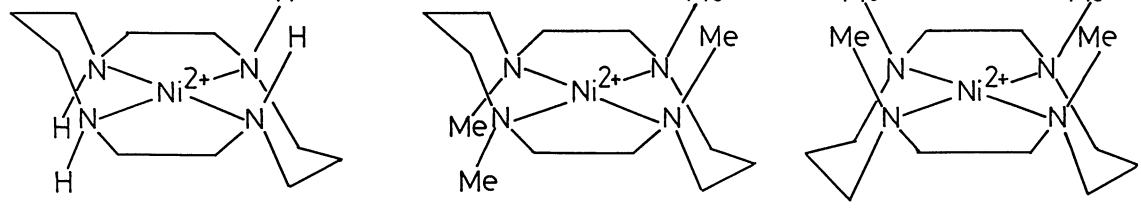
The axial coordination constants for (1*R*,4*S*,8*R*,11*S*)-$[NiL]^{2+}$ in various binary mixed solvents using nitrobenzene (NB) as a diluent were reported previously,[15] and the values obtained were decreased in the order DMF (5.4 $mol^{-1}$ $dm^3$)>dimethyl sulfoxide (DMSO) (3.8)>AN (3.1)>benzonitrile (BzN) (0.4), while in pure solvents, the order was AN (13.4)>DMF (10.8)>DMSO (3.5)>BzN (2.4)>$H_2O$ (1.8).[16] In these cases, the coordination constant of AN molecules is larger than that expected from Gutmann's donor number (DN), because DN of the solvents is decreased in the order DMSO>DMF>$H_2O$>AN>BzN, thus suggesting π-back donation.[15] The first and second coordination constants ($K_{NiS1}$ and $K_{NiS2}$) for (1*R*,4*R*,8*S*,11*S*)-$[NiL]^{2+}$ have not been reported yet. An investigation of $K_{NiS1}$ and $K_{NiS2}$ might help in understanding the strong coordination of AN. Therefore, the stepwise coordination constants for (1*R*,4*R*,8*S*,11*S*)-$[NiL]^{2+}$ and a comparison with the results for (1*R*,4*S*,8*R*,11*S*)-$[NiL]^{2+}$ and $[Ni(cyclam)]^{2+}$ in NB mixtures are reported.

## Experimental

NB, DMF, DMSO, AN, and BzN were purified as described previously.[15,17] $[Ni(cyclam)](ClO_4)_2$, $[Ni(cyclam)](BPh_4)_2$ ($BPh_4$=tetraphenylborate) and (1*R*,4*R*,8*S*,11*S*)-$[NiL](ClO_4)_2$ were prepared according to the published methods.[7–9,15,18] The purities were confirmed by the elemental analyses of the respective complexes. The instrumentation and procedure used for measurements of conductances and spectra are as reported previously.[15,18,19]

## Results and Discussion

NB was selected as the diluent for the donor solvents



(a) [Ni(cyclam)]$^{2+}$ (b) (1R,4R,8S,11S)-[NiL]$^{2+}$ (c) (1R,4S,8R,11S)-[NiL]$^{2+}$

Scheme 1.

because polar NB dissolves (1*R*,4*R*,8*S*,11*S*)-[NiL]$(ClO_4)_2$ enough to permit measurements of the molar absorptivities spectrophotometrically. As NB has a weak basicity, NB is not coordinated to both (1*R*,4*R*,8*S*,11*S*)-[NiL]$^{2+}$ and [Ni(cyclam)]$^{2+}$, and furthermore larger coordination constants of donor solvents were obtained in NB rather than in nitromethane and propylene carbonate.[15,17] Figures 1 (A) and (B) show variations of the visible spectra for (1*R*,4*R*,8*S*,11*S*)-[NiL]$^{2+}$ and [Ni(cyclam)]$^{2+}$ with AN concentration in NB. The wavelength of absorption maximum is 500 and 450 nm for the square-planar species (1*R*,4*R*,8*S*,11*S*)-[NiL]$^{2+}$ and [Ni(cyclam)]$^{2+}$, respectively. In both Figs. 1 (A) and (B) the absorbance decreases with increasing donor solvent concentration.

Figures 2 and 3 show variations of the molar absorptivities for (1*R*,4*R*,8*S*,11*S*)-[NiL]$^{2+}$ and [Ni(cyclam)]$^{2+}$ with the concentration of the donor solvents, respectively. The molar absorptivities for both complexes decreased with increasing donor solvent concentration. It should be noted that the decreasing ratio of AN is larger than those of DMF and DMSO for (1*R*,4*R*,8*S*,11*S*)-[NiL]$^{2+}$, but the reverse is true for [Ni(cyclam)]$^{2+}$. For [Ni(cyclam)]$^{2+}$ a small variation in the molar absorptivities was observed. The plots for BzN in which there is no variation in the molar absorptivities for [Ni(cyclam)]$^{2+}$, are omitted.

Equations 1 and 2 show the stepwise equilibria for the coordination of a solvent to the square-planar complexes,

$$(1R,4R,8S,11S)\text{-}[\mathrm{NiL}]^{2+} + \mathrm{S} \overset{K_{\mathrm{NiS1}}}{\rightleftarrows} (1R,4R,8S,11S)\text{-}[\mathrm{NiL(S)}]^{2+}, \quad (1)$$

$$(1R,4R,8S,11S)\text{-}[\mathrm{NiL(S)}]^{2+} + \mathrm{S} \overset{K_{\mathrm{NiS2}}}{\rightleftarrows} (1R,4R,8S,11S)\text{-}[\mathrm{NiL(S)_2}]^{2+}, \quad (2)$$

where S stands for the donor solvent. The molar absorptivities of the complexes are correlated to the

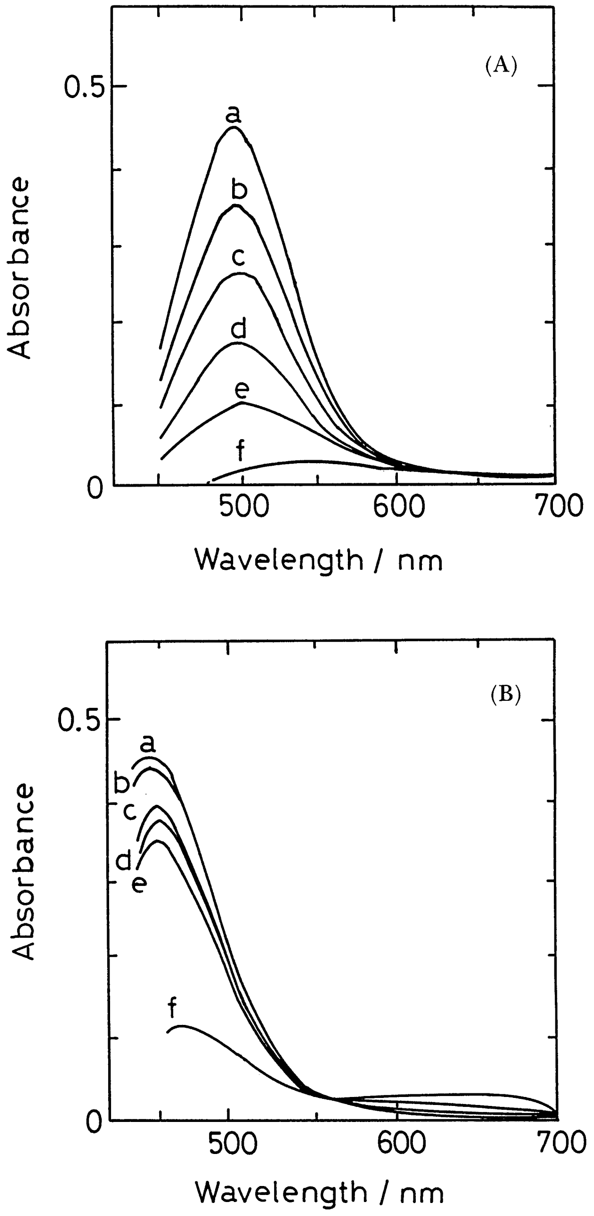


Fig. 1. (A) Variation of the visible spectrum with AN concentration for a solution of (1*R*,4*R*,8*S*,11*S*)-[NiL]$(ClO_4)_2$ ($1\times10^{-3}$ mol dm$^{-3}$) in NB at 25 °C. AN concentration (mol dm$^{-3}$): (a) 0.0, (b) 0.067, (c) 0.13, (d) 0.19, (e) 0.33, (f) neat; (B) for [Ni(cyclam)]$(ClO_4)_2$. AN concentration (mol dm$^{-3}$): (a) 0.0, (b) 0.32, (c) 0.54, (d) 0.71, (e) 1.0, (f) neat.

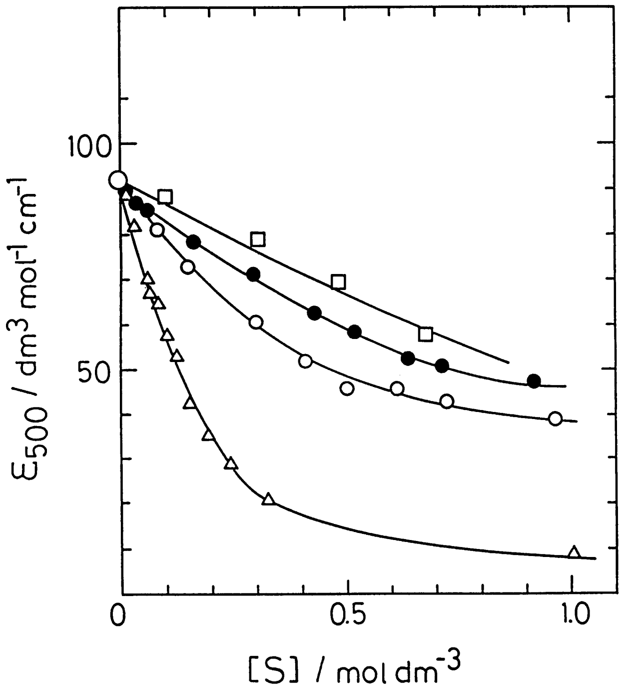


Fig. 2. Variation of molar absorptivities for (1*R*,4*R*,8*S*,11*S*)-[NiL]$^{2+}$ with the donor solvent concentration in NB at 25 °C. ○, DMSO; ●, DMF; △, AN; □, BzN.

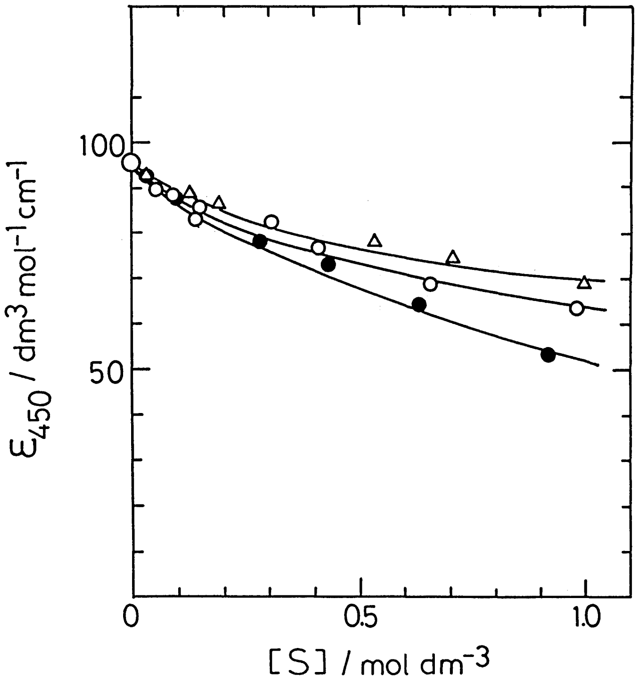


Fig. 3. Variation of molar absorptivities for [Ni(cyclam)]$^{2+}$ with the donor solvent concentration in NB at 25 °C. ○, DMSO; ●, DMF; △, AN.

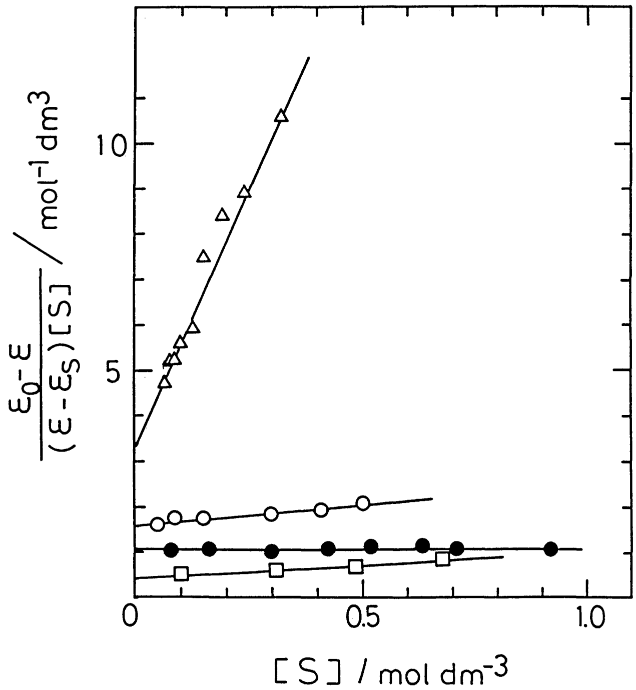


Fig. 4. Plots of $(\varepsilon_o-\varepsilon)/(\varepsilon-\varepsilon_s)$[S] for (1*R*,4*R*,8*S*,11*S*)-[NiL]$^{2+}$. ○, DMSO; ●, DMF; △, AN; □, BzN.

axial coordination constants by Eq. 3.

$$(\varepsilon_o-\varepsilon)/(\varepsilon-\varepsilon_s)[\mathrm{S}]=K_{\mathrm{NiS1}}+K_{\mathrm{NiS1}}K_{\mathrm{NiS2}}\,[\mathrm{S}]. \qquad (3)$$

The molar absorptivity, $\varepsilon_o$ of square-planar species for (1*R*,4*R*,8*S*,11*S*)-[NiL]$^{2+}$ and for [Ni(cyclam)]$^{2+}$ is 92.2 dm$^3$ mol$^{-1}$ cm$^{-1}$ at 500 nm and 94.9 at 450 nm, respectively. The symbol $\varepsilon$ is the apparent molar absorptivity, and $\varepsilon_s$ is the combined molar absorptivity for five- and six-coordinated species and is 1.0 dm$^3$ mol$^{-1}$ cm$^{-1}$ at 500 nm for (1*R*,4*R*,8*S*,11*S*)-[NiL]$^{2+}$ and 14.2 at 450 nm for [Ni(cyclam)]$^{2+}$. A typical plot of Eq. 3 for (1*R*,4*R*,8*S*,11*S*)-[NiL]$^{2+}$ is shown in Fig. 4 where a good linear relationship is obtained for all solvents used. In all the plots of Fig. 4, the concentration of S bonded to the cation is negligible compared with that of unbonded S, since the complex cation concentration used for measurements is $1\times10^{-3}$ mol dm$^{-3}$. The $K_{\mathrm{NiS1}}$ and $K_{\mathrm{NiS2}}$ values can be obtained from the intercept and slope, and the results obtained are summarized in Table 1.

The overall coordination constants for [Ni(cyclam)]($ClO_4$)$_2$ and (1*R*,4*R*,8*S*,11*S*)-[NiL]($ClO_4$)$_2$ in NB are decreased in the order DMF (0.24)>AN (0.22)>DMSO (0.021) and AN (23)>DMSO (0.80)>BzN (0.76)>DMF (0.11), respectively. In pure solvents the overall coordination constants for [Ni(cyclam)]($ClO_4$)$_2$ are decreased in the order DMF (27.15)>AN (8.85)>DMSO (2.13)>$H_2O$ (0.43, 0.38).[20,21]

Coordination ability of DMSO and $H_2O$ as pure solvents is less than that expected from their basicity. This is attributed to the self-association which masks the donor oxygen atom: DMSO forms a cyclic dimer and water forms a three dimensional polymer.[17]

From Table 1, it is obvious that the coordination constants for [Ni(cyclam)]($ClO_4$)$_2$ are smaller than those for (1*R*,4*R*,8*S*,11*S*)-[NiL]($ClO_4$)$_2$. This can be

Table 1. $K_{\mathrm{NiS1}}$ and $K_{\mathrm{NiS2}}$ for (1*R*,4*R*,8*S*,11*S*)-[NiL]$^{2+}$ and [Ni(cyclam)]$^{2+}$, and $K_{\mathrm{NiS}}$ for (1*R*,4*S*,8*R*,11*S*)-[NiL]$^{2+}$ in NB at 25 °C

| Solvent | (1*R*,4*R*,8*S*,11*S*)-[NiL]$^{2+}$ | | [Ni(cyclam)]$^{2+}$ | | (1*R*,4*S*,8*R*,11*S*)-[NiL]$^{2+,a)}$ |
|---|---|---|---|---|---|
| | $K_{\mathrm{NiS1}}$ | $K_{\mathrm{NiS2}}$ | $K_{\mathrm{NiS1}}$ | $K_{\mathrm{NiS2}}$ | $K_{\mathrm{NiS}}$ |
| DMSO | 1.6±0.1 | 0.5±0.1 | 0.7±0.1 | 0 | 3.8 |
| DMF | 1.0±0.1 | 0.1±0.1 | 0.8±0.1 | 0.3±0.1 | 5.4 |
| AN | 3.4±0.3 | 6.7±0.1 | 0.2±0.1<br>0.7±0.1$^{b)}$ | 1.1±0.2<br>1.2±0.1$^{b)}$ | 3.1 |
| BzN | 0.4±0.1 | 1.9±0.1 | — | — | 0.4 |

a) Ref. 15. b) [Ni(cyclam)]($BPh_4$)$_2$.

explained, first, through the phenomenon of hydrogen bonding of the four N-H protons of [Ni(cyclam)]$^{2+}$. Effects of hydrogen bonding of N-H protons on ionic association in NB were studied.[18] The ionic association constants $K_a$ obtained by the Fuoss-Edelson method,[22] were 0, 1190, and 11000 mol$^{-1}$ dm$^3$ for [Ni(cyclam)](BPh$_4$)$_2$, (1$R$,4$S$,8$R$,11$S$)-[NiL](ClO$_4$)$_2$, and [Ni(cyclam)](ClO$_4$)$_2$, respectively, indicating that [Ni(cyclam)](ClO$_4$)$_2$ greatly associative.[15,18] The difference in $K_a$ between BPh$_4^-$ and ClO$_4^-$ for [Ni(cyclam)]$^{2+}$ is slightly reflected on the $K_{NiS1}$ values: the ClO$_4^-$ complex gives a little smaller $K_{NiS1}$ value compared with BPh$_4^-$. The basic donor solvents can be also hydrogen-bonded to the N-H protons, and their attack on the central nickel is hampered.

Secondly, the stability of square-planar configuration for [Ni(cyclam)]$^{2+}$ is considered. The logarithm of the stability constant is 8.6 for (1$R$,4$S$,8$R$,11$S$)-[NiL]$^{2+}$ and 20.1 for [Ni(cyclam)]$^{2+}$.[23] The absorption wavelength of the d-d transition observed is 450, 500, and 520 nm for [Ni(cyclam)]$^{2+}$, for (1$R$,4$R$,8$S$,11$S$)-[NiL]$^{2+}$, and for (1$R$,4$S$,8$R$,11$S$)-[NiL]$^{2+}$, respectively, indicating that the stability for the square-planar configuration decreases in the order [Ni(cyclam)]$^{2+}$>(1$R$,4$R$,8$S$,11$S$)-[NiL]$^{2+}$>(1$R$,4$S$,8$R$,11$S$)-[NiL]$^{2+}$. Cyclam is the secondary amines while L is the tertiary ones. As the coordination of the tertiary amine is stronger than the secondary one, the stability for [NiL]$^{2+}$ must be larger than that for [Ni(cyclam)]$^{2+}$.[23] However, the repulsion between the methyl groups of [NiL]$^{2+}$ leads to less stability for the square-planar configuration. In other words, it is easy for [NiL]$^{2+}$ to change its configuration from the square-planar into the square-pyramidal or the octahedral. Therefore, [NiL]$^{2+}$ easily receives the attack of the solvent.

Table 1 also compiles the coordination constants obtained together with $K_{NiS}$ for (1$R$,4$S$,8$R$,11$S$)-[NiL]$^{2+}$. The $K_{NiS1}$ values of DMF and DMSO are less than $K_{NiS}$, but those of AN and BzN are the same as $K_{NiS}$. The calculation of the strain energy showed that each coordination site for (1$R$,4$R$,8$S$,11$S$)-NiL]$^{2+}$ is more sterically crowded than the coordination site for (1$R$,4$S$,8$R$,11$S$)-[NiL]$^{2+}$.[3,4] It is likely that coordination of DMF and DMSO molecules with -N(CH$_3$)$_2$ and two -CH$_3$, respectively, is sterically hindered, and the rod-like cyano group receives little steric hindrance.

Cyano groups show a striking and different trend from other solvents. $K_{NiS2}$ for AN is twice as large as $K_{NiS1}$, although $K_{NiS2}$ for DMF is only one tenth of $K_{NiS1}$. This anomalous behavior of AN may refer to $\pi$-back donation. Evidence has been reported for the $\pi$-back bonding of AN: the increase of the CN stretching frequency for copper halide adducts with AN,[24] the large stability constant of bis ($\alpha$-furil dioximato)-diiodocobaltate(III) in AN,[25] the large ratio of 10$Dq'$ (nickel bromide AN complex)/10$Dq'$ (nickel chloride AN complex),[26] the dependence of the coordination power value (relative Gibbs free energy change for solvation of the nickel ion) on other parameters,[27] and the deviation of $\nu_{max}$ for the copper complexes in AN from a correlation of $\nu_{max}$ with solvent donor number.[28] In all these cases, AN is strongly bonded to the complex than expected from its basicity. The coordination of one AN molecule via $\pi$-back donation makes another axial trans-coordination site active (a trans-effect). On receiving the electron-pair of AN, the nickel atom loses the positive charge slightly, but when the electrons of the nickel atom flow in the AN molecule via $\pi$-back donation, the density of positive charge on nickel increases. Therefore, the larger the $\pi$-back donation becomes, the stronger the second coordination, resulting in $K_{NiS2}>K_{NiS1}$ for nitriles. The activation enthalpy for the loss of a single solvent molecule from (1$R$,4$R$,8$S$,11$S$)-[NiL(AN)$_2$]$^{2+}$ and (1$R$,4$R$,8$S$,11$S$)-[NiL(DMF)$_2$]$^{2+}$ are 41.5 and 38.3 kJ mol$^{-1}$, respectively.[14] This indicates that the coordination of AN to (1$R$,4$R$,8$S$,11$S$)-[NiL]$^{2+}$ is stronger than that of DMF, thus supporting $\pi$-back donation. In addition, the wavelength of the absorption maximum is 349 and 373 nm for the octahedral species (1$R$,4$R$,8$S$,11$S$)-[NiL(S)$_2$]$^{2+}$ in AN and in DMF, respectively, and indicates blue-shifts in AN compared with DMF.[15]

X-Ray crystallographic data showed that the deformation in the square-planar configuration of (1$R$,4$S$,8$R$,11$S$)-[NiL]$^{2+}$ is larger for one AN molecule coordination than that of DMF,[5,29,30] hence supporting the above view. The Ni-N (ring) bond lengths for the non-coordinated, DMF-coordinated, and AN-coordinated species are 0.1960, 0.2105, and 0.2143 nm, respectively. For DMF-coordinated species the distance of nickel atom displaced from the N$_4$ plane is 0.029 nm, while for the AN-coordinated it is 0.034 nm. The trans non-coordinating axial site of (1$R$,4$S$,8$R$,11$S$)-[NiL(AN)]$^{2+}$ is also activated, but the solvent cannot be coordinated because of the steric hindrance of methylene groups.

Influence of the ligand trans to O$_2$ on the O$_2$ adduct formation for the square-planar complex has already been reported.[31-33] The coordination constants of O$_2$ ($K_{O_2}$) increases in the order H$_2$O<pyridine (Py)<imidazole (Im)<NH$_3$<CN$^-$ for [Co(cyclam)]$^{2+}$, Cl$^-$<ClO$_4^-$<Br$^-$<Py<Im for [Co(Me$_6$(14)4,11-dien N$_4$)]$^{2+}$, and ClO$_4^-$<Cl$^-$<SCN$^-$ for [Co(C-meso-Me$_6$[14]-aneN$_4$)]$^{2+}$. As a matter of fact, when the axial ligand trans to O$_2$ is coordinated to the cobalt atom by $\pi$-back donation (e.g. CN$^-$), the $K_{O_2}$ is large. A correlation between axial ligand basicity and oxygen affinity is stronger for a fully saturated macrocycle than that for unsaturated ones.[31] It is likely that the $\pi$-electrons of the macrocycle interrupt the approaching ligand through repulsion, resulting in a large $K_{NiS2}$ for (1$R$,4$R$,8$S$,11$S$)-[NiL]$^{2+}$ which has a saturated macro-

cyclic ligand.

## Conclusion

The introduction of AN into the coordination sphere of (1*R*,4*R*,8*S*,11*S*)-$[NiL]^{2+}$ is supported by $\pi$-back donation and hence AN is strongly bonded to the nickel atom. Coordination of nitriles by $\pi$-back donation activates the opposite axial trans-site of the square-planar complexes, contrary to DMF and DMSO, where no influence on its trans position is observed. The fact that $K_{NiS2}$ is larger than $K_{NiS1}$ for AN in AN-NB mixture, provides conclusive evidence for $\pi$-back donation to the nickel atom.

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